

1914
Sh8

SHUM

On the Range of
Composition of Portland Cement

Chemistry

B. S.

1914

THE UNIVERSITY
OF ILLINOIS
LIBRARY

1914
Sh8



**ON THE RANGE OF COMPOSITION
OF
PORTLAND CEMENT**

BY

NIM CHI SHUM

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1914



Digitized by the Internet Archive
in 2014

<http://archive.org/details/onrangeofcomposi00shum>

1914
578

UNIVERSITY OF ILLINOIS

May 30th. 1914

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Hsin Chi Shum

ENTITLED *On the Range of Composition
of Portland Cement.*

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF *Bachelor of Science in
Chemistry.*

Ralph N. Hursh.

Instructor in Charge

APPROVED: *W. S. Koyne*

HEAD OF DEPARTMENT OF *Chemistry*



TABLE OF CONTENTS

	Page
I. Development of the Portland Cement Industry.	1
II. Constitution of Portland Cement.	2
III. The Range of Composition.	9
IV. Calculation of the Cement Batch.	11
V. Present Field of Study.	14
VI. Materials and Preparation of Mixtures.	15
VII. Methods and Results of Tests.	20
VIII. Curves.	24
IX. Discussion of Results.	27

On the Range of Composition of Portland Cement.

DEVELOPMENT OF THE PORTLAND CEMENT INDUSTRY.

The construction of the Eddystone Light House in England marked a new era in the hydraulic cement industry. In 1756 when John Smeaton, the engineer, attacked the problem of building this structure, he undertook a series of investigations the result of which was the discovery of a cement material, which not only hardened better in air, but would also harden under water. From the results of his work, the development of Portland cement may be traced.

It was not until 1824 that Portland cement came into existence. This invention is credited to Joseph Aspdin, a brick-layer of Leeds, England. He took out a patent on an improved cement which he proposed to make from the dust of roads repaired with limestone, or else from limestone itself combined with clay, by burning and grinding. This cement he called "Portland cement" because, when hardened, it produced a yellowish gray mass resembling in appearance the stone from the famous quarries of Portland, England.

In the United States the cement industry first began with the discovery, in 1818, of a natural cement rock near Chittenango, Madison County, New York, by Mr. Canvass White, an engineer engaged in the construction of the Erie Canal. However, the Portland cement was not made until 1875. Mr. David O. Sayler,

president of the Coplay Cement Company, noticed that the harder burned portions of his Rosendale clinker gave a cement which for a short period would show a tensile strength equal to that of the best imported Portland, but this cement would crumble away as time went on. This was due to the fact that the raw materials were not properly proportioned. Sayler finally succeeded in making a good Portland cement by mixing a certain amount of cement rock high in lime with his ordinary cement rock. Thus, the Coplay Cement Company produced the first Portland cement in America.

CONSTITUTION OF PORTLAND CEMENT.

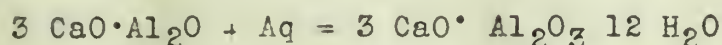
Following the invention of artificial hydraulic cement by John Smeaton, many theories had been advanced on this subject by various investigators. In 1887, the work of Le Chatelier¹ opened up a new method of investigation showing the whole matter in a new light. He was the first to undertake a mineralogical study of the constitution of Portland cement by means of the microscope. He identified four minerals in a glassy mass forming the cement clinker, (1) colorless, double refracting, cubical crystals, later called alite by Törnebohm- (2) between these a darker substance, double refracting, but without crystalline structure, celite- (3) slightly yellowish crystals, opaque and striated, called belite- (4) very small crystals with rather strong double refraction, felite. These were contained in a glassy mass which had no influence upon polarized light.

Le Chatelier considered "alite" as $3 \text{ CaO} \cdot \text{SiO}_2$, the active ingredient of cements, which hydrated according to the reaction

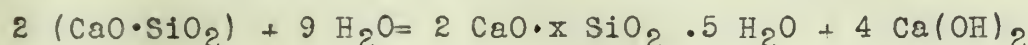
.....
1. Le Chatelier- The Constitution of Hydraulic Mortars, tr. by Mack

$3 \text{ CaSiO}_2 + \text{Aq} = \text{CaO} \cdot \text{SiO}_2 \cdot 2.5 \text{ H}_2\text{O} + 2 \text{ Ca} (\text{OH})_2$. His analysis showed 1.7 to 1.8 equivalent of CaO to 1 of SiO_2 , considerably more than the mono-silicates. He explained this by the theory that a part of the CaO was freed after hydration and held by capillary attraction.

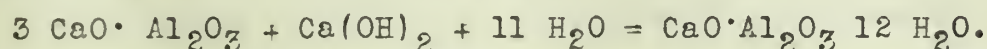
In addition to the tri-calcium silicate, the tri calcium aluminate was found.



The hydration of the cement Le Chatelier expressed by two reactions:



followed by the reaction forming a basic aluminate,



The hydrated basic aluminate determines the setting of the cement while the hardening is fixed by the tri-calcium silicate. Le Chatelier fixed the amount of lime necessary by the relation

$$\frac{\text{CaO}}{\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3} > 3$$

where the substances are represented in equivalents. The upper limit was, fixed at,

$$\frac{\text{CaO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3} < 3$$

In 1897 Törnebohm² corroborated the petrographic work of Le Chatelier. He did not know of Le Chat^uelier's work and investigated different clinker. According to his conclusions the alite was an isomorphous mixture of tri-calcium silicate with the

.....
2. Törnebohm- Über die Petrographie des Portlandzements,-
Stockholm 1897.

aluminate, $9 \text{ CaO} \cdot 2 \text{ Al}_2\text{O}_3$. The cement formula he expressed as $x (3 \text{ CaO SiO}_2) + 9(\text{CaO} \cdot 2 \text{ Al}_2\text{O}_3)$ where x fluctuates around 9. The minerals were separated by means of the Thoulet solution.

In 1898 S. B. and W. B. Newberry³ studied the question by fusing synthetic mixtures of CaO and SiO_2 . A product was obtained, which hardened like the best cement. Showing the ratio of CaO to SiO_2 in the tri-calcium silicate as 2.8 to 1 by weight and in the aluminate, $2 \text{ CaO} \cdot \text{Al}_2\text{O}_3$ as 1.1 CaO to 1 Al_2O_3 by weight they derived a formula showing the maximum CaO content of a correctly proportioned Portland cement. $\% \text{ CaO} = \% \text{ SiO}_2 \times 2.8 + \% \text{ Al}_2\text{O}_3 \times 1.1$. Cement prepared with lime, alumina, and silica proportioned according to the above formula gave good results, whereas that prepared by Le Chatelier's formula was unsound, showing the lime to be in excess.

In 1897 Liamin⁴ showed by micro-photographs the interlacing crystals of lime hydrate and lime alumina silicates in hardened cement. The main constituent according to Liamin was the lime hydrate.

In 1898 Rebuffat⁵ divided cements into two classes, viz.:

1. Cement of simple, compact structure, non-crystalline, derived from a mixture of calcium oxide, silicate, and aluminate. These comprise the hydraulic limes and quick setting cements.

2. Cements of crystalline structure derived from a combination of a crystalline mass, consisting of $2 \text{ CaO} \cdot \text{SiO}_2$ and CaO and the

.....
3. S. B. & W. B. Newberry- Tonind. Ztg. 1898- p. 878.

4. Liamin- Report of the Imperial Russian Technical Society, 1897

5. Rebuffat- Gazz. chim. Ital. 28 II (1898)

calcium aluminate in various proportions,—Portland cements and cements high in silica. The quantitative constitution of the various hydraulic cements after setting, he assumes, is the same, a mixture of Ca(OH)_2 , hydrated calcium silicate and hydrated calcium aluminate with some accessory ingredients.

In 1902 Meyer⁶ produced tri-calcium silicate in mixtures without Al_2O_3 , using Fe_2O_3 and MnO_2 as fluxes. He does not believe that the di-calcium silicate can exist in the presence of free lime and that the tri-calcium silicate can only be produced by crystallization from a fused magma. The tri-calcium silicate hydrates to $2 \text{ CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$, which loses half the water at 160°C . while Ca (OH)_2 dehydrates at a much higher temperature. The process of hydration, according to Meyer, is represented as,

$$2 (3 \text{ CaO}) \cdot \text{SiO}_2 + \text{Aq} = 2 (2\text{CaO}) \cdot \text{SiO}_2 \cdot \text{H}_2\text{O} + 2\text{Ca (OH)}_2.$$

In 1903 Rohland⁷ considered the cement clinker as a solution of CaO in silicates. Later work was done by Rohland upon the effect of positive and negative catalysers on the time of setting of cements.

In 1902 Clifford Richardson⁸ prepared tri-calcium

.....

6. Meyer- Protokoll der Generalversammlungen des Vereins Deutscher Portlandzement fabrikanten, 1901

7. Rohland- Der Portlandzement vom phys.- chem. Stand punkte. Leipzig, 1903.

8. The Constitution of Portland Cement
Cement 5, 316, (1904)

silicate synthetically by fusion in the oxyhydrogen flame as well as non-dusting di-calcium silicates, both hardening in moist air and water. By means of micro-photographs. he showed the crystalline character of portland cement and defined it as a solid solution.

Bates⁹ assumes that the following compounds may exist in Portland cement, tri-calcium silicate, di-calcium silicate, calcium aluminates in which the CaO and Al_2O_3 are combined in ratios of 3 to 1, 5 to 3 or 1 to 1 and free lime. Other compounds may be formed between CaO , Al_2O_3 , Fe_2O_3 and SiO_2 but are scarcely to be found in Portland cement.

Mono-calcium- silicate or meta-calcium silicate, $\text{CaO} \cdot \text{SiO}_2$. It is the only anhydrous calcium silicate occurring in nature. Le Chatelier and Kauster believed it might be produced also by the wet process, finding the composition to be CaO , SiO_2 , 1.1 H_2O . Le Chatelier considered it the only silicate liable to form during the hardening of current. $\text{CaO} \cdot \text{SiO}_2$ possesses hydraulic properties. It is formed at low temperatures and is the principal hydraulic constituent of pozzuolane cement.

The Di-calcium Silicate- The di-calcium silicate is the compound to which generally the disintegrating or dusting of imperfectly proportioned Portland cement is attributed. Zulkowski,¹⁰ Le Chatelier, and also Unger invariably failed to obtain a stable product in fusing a mixture of calcium oxide and silica in the molecular proportions of 2 to 1. They always obtained a compound which crumbled into dust upon cooling in the air or under mercury.

9. The Constitution of Portland Cement, P. H. Bates- Cement and Eng'g. News, V. 25-p. 46.

10. Zulkowski- Erhaltungstheorie d. Hydraulische Bindemittel, Berlin, 1901.

Zulkowski observed that disintegration could be prevented, if the red hot fused product was chilled quickly by dropping it into water. Zulkowski explained it by the existence of two isomeric compounds, an ortho-silicate and a meta-silicate, whereas Le Chatelier attributed it to dimorphism and Hawit assumed that the di-calcium silicate existed in two allotropic modifications. Michaelis¹¹ declared that, in addition to a faulty chemical composition, burning at too high a temperature was responsible for the disintegration of certain Portland cement mixtures. On the other hand F. Schott¹² put the blame upon imperfect combination of the raw materials, caused by insufficient grinding and mixing, and maintained that a stable di-calcium silicate existed. The temperatures at which the experimenters obtained the product differed considerably. Zulkowski burnt a slightly sintered di-calcium silicate at the melting point of Seger cone 21. Le Chatelier believed that he obtained a fused di-calcium silicate at the melting point of iron. Rohland stated its melting point to be 1740 centigrade. Shepherd and Rankin¹³ show that $2 \text{ CaO} \cdot \text{SiO}_2$ exists in four distinct crystal forms. In changing from the β to the γ form at about 675°C . there is a 10% volume increase which causes the dusting of clinker containing much of this compound. The ortho-silicate is not hydraulic.

.....

11. Michaelis- Die Hydraulischen Mörtel Leipzig, 1869.

12. F. Schott- Dingl. Polyt. Jour. 202, 434 and 513.

13. Shepherd & Rankin- Jr. Ind. & Eng'g. Chem.
Vol. 3, No. 4 (1911)

The transformation from the beta to the gamma form is largely prevented by increase of Fe_2O_3 in a cement since it enters the ortho-silicate, coloring it brown.

Tri Calcium Silicate- A great deal of discussion may be found relative to the existence or non-existence of the compound, $3 \text{CaO} \cdot \text{SiO}_2$. In their careful study of the binary system $\text{CaO}-\text{SiO}_2$ Day and Shepherd were unable to produce such a compound but the later study made on the ternary system, $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ resulted in the production of very pure crystals of the tri-calcium silicate. In the presence of small amounts of Al_2O_3 the compound readily appeared and the fact of its existence as the essential hydraulic compound in Portland cement has been established beyond question. The tri-calcium silicate is unstable at its melting point dissociating to form $2 \text{CaO} \cdot \text{SiO}_2$ and CaO . In Portland cement clinker the presence of Al_2O_3 and fluxes aids materially in producing considerable amounts of $3 \text{CaO} \cdot \text{SiO}_2$. The amount of the compound which is found in the clinker seems to increase with the temperature of burning.

The $\text{CaO}-\text{Al}_2\text{O}_3$ Series- In this series the compounds which have been observed are CaO , $3 \text{CaO} \cdot \text{Al}_2\text{O}_3$, two forms of $5 \text{CaO} \cdot 3 \text{Al}_2\text{O}_3$, the one stable, the second unstable, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, two forms of $3 \text{CaO} \cdot 5 \text{Al}_2\text{O}_3$, a stable form and an unstable form, and Al_2O_3 . $3 \text{CaO} \cdot \text{Al}_2\text{O}_3$ (CaO 62.22, Al_2O_3 37.78).- This compound is not stable at its melting point and perfectly homogeneous preparations of this composition, free from grains of crystallized CaO and $5 \text{CaO} \cdot 3 \text{Al}_2\text{O}_3$ have never been obtained. The tri-calcium aluminate is formed in Portland cement clinker and acts as a hydraulic compound, hardening quickly but high alumina cements are likely to decrease

in strength in time.

Calcium Ferrites- The nature and properties of the calcium ferrites are not well known. Fe_2O_3 seems to take an important part in reducing the burning temperature of cement clinker and some of its compounds with calcium are hydraulic. It may partially and perhaps wholly replace the Al_2O_3 as shown by the iron ore cement. The calcium ferrites were produced mainly with a view to ascertain whether they have to be regarded as hydraulic substances or whether the iron oxide contained in cements has merely to be considered as an adulteration. With regard to the iron constituent of the Portland cement clinker, P. H. Bates¹⁴ statement may be quoted as follows

"It has been found almost invariably that the iron oxide exists in three different forms. No matter whether the clinker be well-burned or under-burned, or whether it contains a high or low percentage of lime, the iron oxide always enters into the beta orthosilicate. The grains of the latter are colored brownish to red. When the 5 to 3 lime aluminate is present, it also colors it, but it has not been noticed to color either the trisilicate or tri-aluminate. It also occurs in the interstices between the other cement minerals. In the case of low lime cements, this interstitial material is double refracting, has an index of refraction greater than 1.75 and seems to correspond optically to the compound $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$. With the very high lime content cements and higher burned cements, this compound disappears and instead there is formed an almost opaque glass and a small amount of magnetite."

RANGE OF COMPOSITION-

Portland cement is an artificial silicate produced by intimately blending clayey and calcareous materials, burning them to vitrification, and grinding the resultant slag-like mass to a fine powder. This powder, if of the proper composition, will hy-

.....

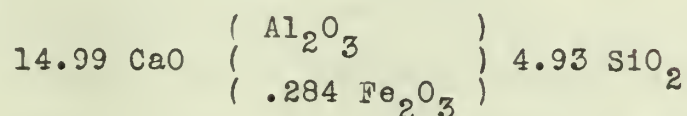
14. P. H. Bates, Cement & Eng'g. News, V. 25- p. 47

drate and harden in water to a stone-like mass, of practically constant volume, which shows considerable tensile and crushing strength and is able to cement together relatively large quantities of sand.

The composition of Portland cement of good quality is usually within the following limits.

	Limits	Average
Silica	19-26%	22%
Alumina	4-11%	7.5%
Ferric oxide	2- 5%	2.5%
Lime	58-67%	62.%
Magnesia	0- 5%	2.5%
Sulphuric acid	0-2.5%	1.5%
Alkalies	0-3%	2. %

The average American Portland cement may be calculated to the ceramic body formula-



The alumina is reduced to unity as a ready means of comparing the composition to the clay base since the fundamental formula of clay substance is given as $\text{Al}_2\text{O}_3 \cdot 2 \text{ SiO}_2 \cdot 2 \text{ H}_2\text{O}$. In the above cement formula the clay base is represented by $\text{Al}_2\text{O}_3 \cdot .284 \text{ Fe}_2\text{O}_3 - 4.93 \text{ SiO}_2$ showing 2.93 molecules of free SiO_2 as compared with the kaolinite formula. As there is always a certain amount of feldspathic and micaceous matter in impure clays the actual amount of free SiO_2 is generally considerably less. The oxygen ratios between CaO , Al_2O_3 and SiO_2 are 3.04:0.69:2 making the cement equivalent to a sub-silicate of calcium.

CALCULATION OF THE CEMENT BATCH-

Several formulae have been devised for the calculation of the proportions of clay and lime bearing ingredients of the cement batch.

The Chatelier Formula- American cement chemists make extensive use of the limiting Chatelier formula, as modified by Newberry:

$$x (3 \text{ CaO} + \text{SiO}_2) + y (2 \text{ CaO} + \text{Al}_2\text{O}_3) \quad \text{or} \\ (3x + 2y) \text{ CaO} + x \text{ SiO}_2 + y \text{ Al}_2\text{O}_3$$

Assume a clay of the formula $\text{Al}_2\text{O}_3 \cdot .22 \text{ Fe}_2\text{O}_3 \cdot 5 \text{ SiO}_2 \cdot 2 \text{ H}_2\text{O}$ and pure limestone as ingredients. One part of clay introduces 1 Al_2O_3 and 5 $\text{SiO}_2 = y$ and x respectively. This requires $3x + 2y$ or $15 + 2 = 17$ CaO giving a cement formula $17 \text{ CaO} \left(\begin{smallmatrix} \text{Al}_2\text{O}_3 \\ .22 \text{ Fe}_2\text{O}_3 \end{smallmatrix} \right) 5 \text{ SiO}_2$. The equivalent weight of the clay (the sum of the molecular parts in the formula) is 473.2; of the limestone, 100. The proportions of stone and clay then are 1700: 437.2 or 3.59:1.

Meyers' method- Meyer⁶ advises the use of the formula:

$$x (3 \text{ CaO}) \text{ SiO}_2 + y (n \text{ CaO}) \text{ SiO}_2 \text{ R}_2\text{O}_3,$$

in which the value of $n = 3$ to 4. This is highly commended by some European chemists. This formula has also been stated in the form: $a \text{ M O} + b \text{ Al}_2\text{O}_3 + 1 \text{ SiO}_2$, in which MO is the sum of the equivalents of lime, magnesia, iron oxide and alkalies. The minimum value of $a = 3$, and the maximum value $= 3+b$, where b is the equivalent of alumina.

Hydraulic Modulus- This method is generally used in Europe and also in the United States. It may be stated as follows:

$$n = \frac{\text{Per cent. calcium oxide}}{\text{Per cent. silica} + \text{per cent. alumina} + \text{percent ferric oxide}} = 2$$

The permissible variations of n range from 1.8 to 2.2. Let the sum of the percentages, $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{SiO}_2$ or "silicate" in the clay base be represented by S and the CaO content of the clay be c . The CaO of the clay requires $\frac{c}{n}$ parts of silicate leaving available silicate $= S - \frac{c}{n}$ which requires $n(s - \frac{c}{n})$ parts of CaO . Let S_1 represent the amounts of "silicate" ($\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{SiO}_2$) and c_1 the CaO in the limestone. The silicate requires ns_1 parts of CaO leaving $(c_1 - ns_1)$ % of CaO available. The limestone required to supply the CaO for the clay will then be

$$\frac{n(s - \frac{c}{n})}{c_1 - ns_1} = \frac{ns - c}{c_1 - ns_1}$$

This method is in very general use for calculation of the mixture from day to day in cement plants, where the materials vary only slightly in composition.

Newberry Formula- This is merely a statement of the maximum content of CaO for a well balanced Portland cement,
 $\% \text{CaO} = \% \text{SiO}_2 \times 2.8 + \% \text{Al}_2\text{O}_3 \times 1.1.$

Bleiningger Formula- From the results of his work, Bleiningger¹⁵ concludes that for dry ground mixtures the formula $(2.8 \text{ CaO}) \cdot \text{SiO}_2 + (2 \text{ CaO}) \cdot \text{Al}_2\text{O}_3$ is the safest, using a ratio

$$\frac{\% \text{SiO}_2}{\% \text{Al}_2\text{O}_3} = 3.1 \text{ to } 4.1$$

.....

15. Bleiningger- The Manufacture of Hydraulic Cements, Bull. #3 Ohio Geol. Survey, 1903.

This would correspond to the proportion, in parts by weight, of 1 part of silica to 2.61 parts of lime, or 1 part of silica to 4.66 parts of calcium carbonate. A cement made from a silicious clay and limestone would be decidedly unsafe with the theoretical tri-calcium silicate formula. From his results, however, no deductions can be drawn with reference to the theoretical silicates present in the cement. The work seems to support the views of Vogt that we are dealing with a slag whose limits of composition are not as narrow as they might be supposed. At the same time, there are quite definite limits, for with a formula of $(2.6 \text{ CaO}) - \text{SiO}_2$, $(2 \text{ CaO}) \text{ Al}_2\text{O}_3$, hydraulicity practically ceased and "dusting" began. No coal ash was added to these cements at all, since they were not in contact with coal. The following criticisms may be made on the above formulae:

The Chatelier formula does not give entire satisfaction. For instance, taking the formula- 17 CaO , 5 SiO_2 , Al_2O_3 , $0.22 \text{ Fe}_2\text{O}_3$, the percentage composition is found to be:

Lime	68.54%
Silica	21.60%
Alumina	7.34%
Ferric oxide	2.53%

It will be noticed that the content of lime is higher than that of the average Portland cement.

The formula- $x(3 \text{ CaO} + \text{SiO}_2) + y(2 \text{ CaO} + \text{Al}_2\text{O}_3)$ is inherently wrong when applied indiscriminately in practical work, and must be corrected either by a change in the molecular proportions or by the use of a constant for the various degrees of acidity of the clays.

Meyers' formula was found successful and is highly commended by some European chemists.

Hydraulic Modulus Method- This formula is much cruder and more inaccurate than the Chatelier formula, as it does not discriminate between the three constituents in the denominator. The requirements of the formula would be met equally well by a highly aluminous clay or silicious iron ore. However, it gives a readily available check on the other methods provided a suitable clay is being used and is excellent for routine batch calculations in the plant.

Newberry found that cement prepared synthetically with lime, alumina, and silica proportioned according to his formula gave good results.

Bleininger's Formula- The objection might be made that the formula would give too low a lime content owing to the introduction of silica and alumina in the ash from the coal when burnt in the rotary kiln. There is some justice in this objection, as the tendency of the ash will be to lower the lime content, and undoubtedly some reaction takes place.

In Fig. 1 is shown the triaxial diagram of the system, $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ as given by Shepherd and Rankin. The enclosed area $vxyz$ is suggested by them as the probable field of Portland cement composition. The small rectangle ^{EFGH}_A represents the field of good cements as found by Bleininger.

PRESENT FIELD OF STUDY-

In the present work a study is made of the effect of varying proportions of CaO , Al_2O_3 , and SiO_2 on the properties of

Portland cement. In order to eliminate differences due to varying amounts of Fe_2O_3 and alkalis introduced by varying the clay base in the batches a ball clay low in Fe_2O_3 and alkalis was used with ground quartz for the additional SiO_2 and pure CaCO_3 for the limestone. Enough Fe_2O_3 was added to make 3% of the finished cement in each case and 2% of Na_2CO_3 was added to the raw mixture.

Although it is known that the properties of the cement depend considerably upon the mineralogical make-up of the raw batch it was hoped by a longer burning period to obtain results more or less comparable to those which might be obtained by using a ferruginous clay in the mixture. It was necessary to reduce the variables as far as possible and the use of pure materials probably gives more reliable data in the present case.

Fifteen mixtures were made up with varying proportions of CaO , Al_2O_3 , and SiO_2 as shown in the following table. The three components are calculated to 100%, the Fe_2O_3 and alkali being of constant value throughout the series. This allows the field of work to be shown on a triaxial diagram, Fig. 2.

MATERIALS AND PREPARATION OF MIXTURES.

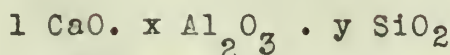
The materials used in preparation of the raw mixtures are as follows:

Whiting	55.10% CaO
Tennesseess Ball Clay	50.20% SiO_2 36.80% Al_2O_3
Ground Potter's Flint	100.00% SiO_2
Hematite	100.00% Fe_2O_3
Soda Ash	100.00% Na_2CO_3

	% Ca O Si O ₂ Al ₂ O ₃				% Si O ₂ Al ₂ O ₃	% Ca O Si O ₂	moles. moles		Molecular ratio.		Formula	
	Ca O	Si O ₂	Al ₂ O ₃	%			Ca O	Si O ₂	Al ₂ O ₃	Si O ₂ Al ₂ O ₃		Ca O Si O ₂
1	69.2	25.2	5.6	4.5	2.746	1	.339	.0438	7.74	2.696	7.74	2.699
2	68.0	25.0	7.0	3.571	2.72	1	.3384	.0565	6.08	2.5	6.08	2.50
3	67.0	24.0	9.0	2.66	2.8	1	.343	.0738	4.54	2.545	4.59	2.54
4	67.0	23.0	10.0	2.3	2.90	1	.322	.082	3.9	2.6	3.90	2.60
5	68.0	24.0	8.0	3.0	2.83	1	.329	.0654	5.1	2.643	5.10	2.64
6	70.0	24.0	6.0	4.0	2.91	1	.315	.0463	6.8	2.831	6.10	2.83
7	71.0	24.0	5.0	4.8	3.	1	.315	.039	8.1	2.43	8.10	2.43
8	72.0	23.0	5.0	4.6	3.13	1	.3	.038	7.8	3.1	7.80	3.10
9	71.0	23.0	6.0	3.83	3.1	1	.3	.0463	6.5	3.	6.50	3.00
10	69.0	23.0	8.0	2.9	3.	1	.316	.0654	4.9	2.8	4.90	2.80
11	68.0	22.0	10.0	2.2	3.1	1	.3	.08	3.7	2.8	3.70	2.80
12	70.0	22.0	8.0	2.75	3.18	1	.29	.063	4.63	3.	4.63	3.00
13	72.0	22.0	6.0	3.7	3.27	1	.29	.047	6.2	3.2	6.20	3.20
14	71.0	21.0	8.0	2.6	3.4	1	.276	.0617	4.46	3.18	4.46	3.18
15	69.0	21.0	10.0	2.1	3.3	1	.284	.079	3.45	2.96	3.45	2.96

The raw batches were calculated from the proportions of CaO , Al_2O_3 and SiO_2 in the table.

For the purposes of comparison the mixtures, it was calculated to the formula.-



For example, taking the first batch, whose composition is 69.2% CaO , 25.2% SiO_2 , 5.6% Al_2O_3

$$\frac{69.2}{56} = 1.235 \text{ CaO}$$

$$\frac{25.2}{60} = .418 \text{ SiO}_2$$

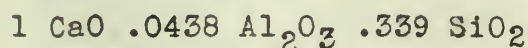
$$\frac{5.6}{102} = .054 \text{ Al}_2\text{O}_3$$

$$\frac{69.2 \times 100}{56} = 123.500 \text{ CaCO}_3$$

$$\frac{.418}{1.235} = .339 \text{ mol. SiO}_2 = y$$

$$\frac{.054}{1.235} = .0438 \text{ mol. Al}_2\text{O}_3 = x$$

The composition may be reduced to the molecular formula,-

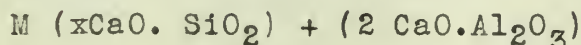


$$.054 \times 2 = .108 \text{ CaO for Al}_2\text{O}_3$$

$$1.235 - .108 = 1.127$$

$$\frac{1.127}{.418} = 2.696 \quad \frac{.418}{.054} = 7.74$$

The batch was then reduced to the formula,



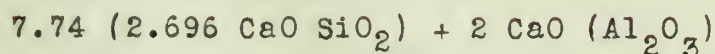
Calculating the percentage and molecular ratios-

$$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}, \frac{\text{CaO}}{\text{SiO}_2} \text{ in the above case}$$

$$\frac{\text{SiO}_2 \quad .418}{\text{Al}_2\text{O}_3 \quad .054} = \frac{\quad}{\quad} = 7.74 \text{ mol. ratio} = m$$

$$\frac{\text{CaO}}{\text{SiO}_2} = \frac{1.127}{.418} = 2.696 \text{ mol. ratio} = x$$

The resulting formula of the mix is



The batch weights were then calculated from the above formula.

$$\frac{36.80}{102} = .36 \text{ Al}_2\text{O}_3$$

$$\frac{50.20}{60} = .836 \text{ SiO}_2$$

$$.36 \times 2 \times 100 = 72 \text{ CaCO}_3 \text{ for Al}_2\text{O}_3$$

$$4.5 \times 36.80 = 165.60 \text{ SiO}_2 \text{ required}$$

$$165.60 - 50.2 = 115.40 \text{ SiO}_2 \text{ as flint}$$

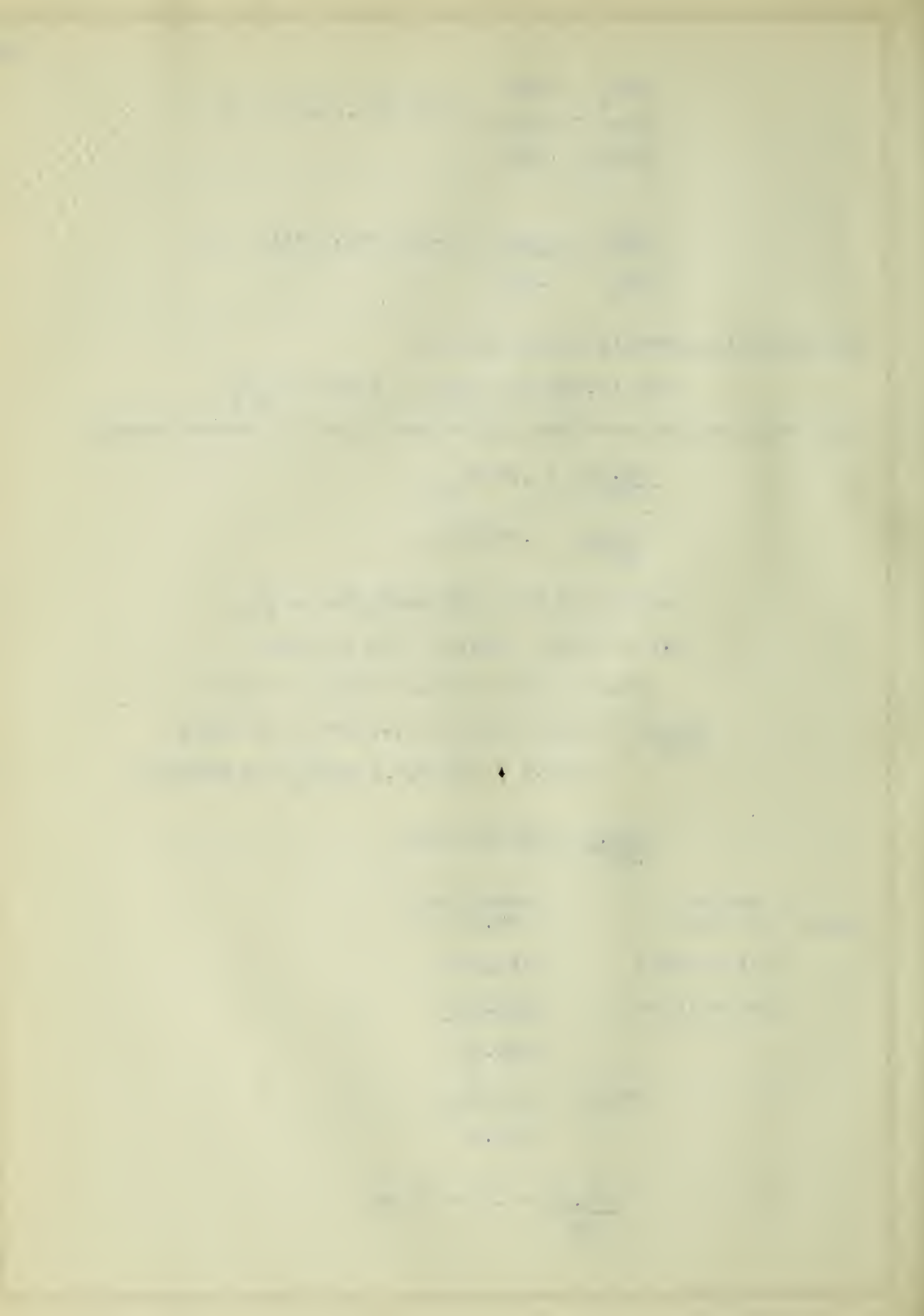
$$\frac{165.60}{60} \times 2.696 \times 100 = 744.1 \text{ CaCO}_3 \text{ for SiO}_2$$

$$744.1 + 72 = 816.1 \text{ CaCO}_3 \text{ for whiting}$$

$$\frac{816.1}{.983} = 832 \text{ whiting}$$

Batch	Raw Wt.	burned wt.
	100 Clay	= 87.00
	115.4 flint	115.40
	832 whiting	<u>458.53</u>
		660.93
	Fe ₂ O ₃	<u>20.44</u>
		681.37

$$\frac{660.93}{97} \times .03 = 20.44$$



Batches amounting to approximately 4500 gms each of burned cement were made up, the raw batches being calculated as follows,- Dividing 4500 by the figure representing the burned weight of the calculated batch, then multiplying the batch weights by this factor gives a batch which when burned weighs 4500 gms.

$$\text{Thus } \frac{4500}{681.37} = 7$$

$$\text{clay} = 100 \times 7 = 700 \text{ gms.}$$

$$\text{Flint} = 115.4 \times 7 = 807.8 \text{ gms.}$$

$$\text{whiting} = 832 \times 7 = 5824.0 \quad "$$

$$\text{Fe}_2\text{O}_3 = 20.44 \times 7 = 143.08 \quad "$$

With an addition of 2% Na_2CO_3 for each batch.

700.0	
807.8	
5824.0	
<u>143.1</u>	
7475.0	

$$74750 \times \frac{2}{100} = 149 \text{ gms. } \text{Na}_2\text{CO}_3$$

The raw materials were weighed out, and the mixture, which had been previous^{ly} pulverized, was ground in a ball mill for about four hours. The well-mixed powder was removed from the mill, slightly moistened with water, and moulded into small briquettes by means of a hand-power dry press. The briquettes were burned in fire-clay chambers in a down-draft, coal-fired test kiln so arranged that the burned clinker could be withdrawn at the finishing temperature and cooled quickly. Samples were drawn out at intervals to examine the clinker. It was found that at cone 16 all the clinkers attained a dark gray color. All the clinkers showed "dusting" except batch 6. Batches 9, 10, 11 and 12 did not dust as badly as the rest of the batches.

The burned clinkers were aged for a week, then crushed in a small jaw crusher, and finally ground in a ball mill until 92% would pass the 100 mesh sieve and 75% the 200 mesh.

METHODS AND RESULTS OF TESTS

Normal consistency, U. S. Government Specification- 100 grams of powdered cement was weighed out, quickly mixed with water and formed into a ball about two inches in diameter. The ball was dropped upon a hard, smooth and flat surface from a height of two feet. The proper consistency was obtained when the ball so dropped did not crack nor flatten out more than one-half of its original diameter. The following table shows the results of each batch.

Normal Consistency	
No.	% of water required
1.	37.8
2.	37.5
3.	41.0
4.	38.2
5.	35.2
6.	33.2
7.	35.0
8.	31.3
9.	35.7
10.	40.0
11.	37.8
12.	37.8
13.	36.2
14.	34.2
15.	41.1

Constancy of volume, U. S. Government Specification-

From each batch two pats of neat cement paste of normal consistency were made up on glass plates, the pats being about 3 inches in diameter, one-half inch in thickness at the center, and tapered to a thin edge. After keeping in moist air for a period of 24 hours, the pats were exposed to steam at atmospheric pressure above boiling water for 3 hours. Batch 6 remained firm and fairly hard, with no signs of cracking, distortion or disintegration. Batches 9, 10, 11, and 12 showed slight cracking and were soft, but no distortion or disintegration was noted, while the rest of the batches were badly cracked, soft, and slightly disintegrated.

Time of Setting- The time of setting was determined by the standard Gilmore needles. A pat of neat cement paste about 3 inches in diameter and one-half inch in thickness with the top flattened was mixed at normal consistency. It was kept in moist air at a room temperature (21°C) and tested from time to time. The cement was considered to have acquired its initial set when the pat would bear, without appreciable indentation, a needle one-twelfth of an inch in diameter loaded to weigh one-fourth of a pound. The final set was acquired when the pat would bear, without appreciable indentation, a needle one-twenty-fourth of an inch in diameter, loaded to weigh one pound. In making the test the needle was held in a vertical position and applied lightly to the surface of the pat. The following table gives the results of these tests:-

Time of Setting

No.	Initial set in min.	Average	Final Set in hrs.	Average
1.	83 80	81.5	9.45 9.58	9.51
2.	92 94	93	9.10 9.6	9.8
3.	37 36	36.5	8.45 8.40	8.42
4.	59 59	59	9.15 9.11	9.13
5.	97 98	97.5	8.3 8.0	8.1
6.	40 39	39.5	9.0 8.50	8.55
7.	81 81	81	10.3 10.7	10.5
8.	85 86	85.5	10.1 9.50	9.55
9.	63 63	63	8.35 8.38	8.37
10.	32 31	31.5	7.23 7.20	7.22
11.	29 30	29.5	6.47 6.50	6.48
12.	32 31	31.5	7.31 7.28	7.30
13.	70 70	70	9.24 9.30	9.27
14.	77 77	77	9.1 9.7	9.4
15.	51 51	51	7.42 7.38	7.40

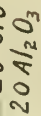
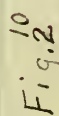
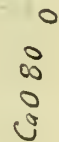
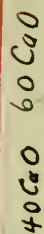
Tensile Strength- Standard tensile test briquettes of neat cement were moulded in brass molds having a cross section of one square inch at the middle. One hundred grams of cement was weighed out and immediately worked up to the normal consistency. The paste was placed in a mould, pressed firmly by fingers and smoothed off with a trowel. The mould was turned over and smoothed off. After standing for a few minutes, the briquette was removed from the mould and allowed to stand in moist air for twenty-four hours. The briquette was then immersed in water at a constant temperature (21°C.) for a period of six days. The briquette was tested in a standard tensile test machine. The results are recorded in the following table:

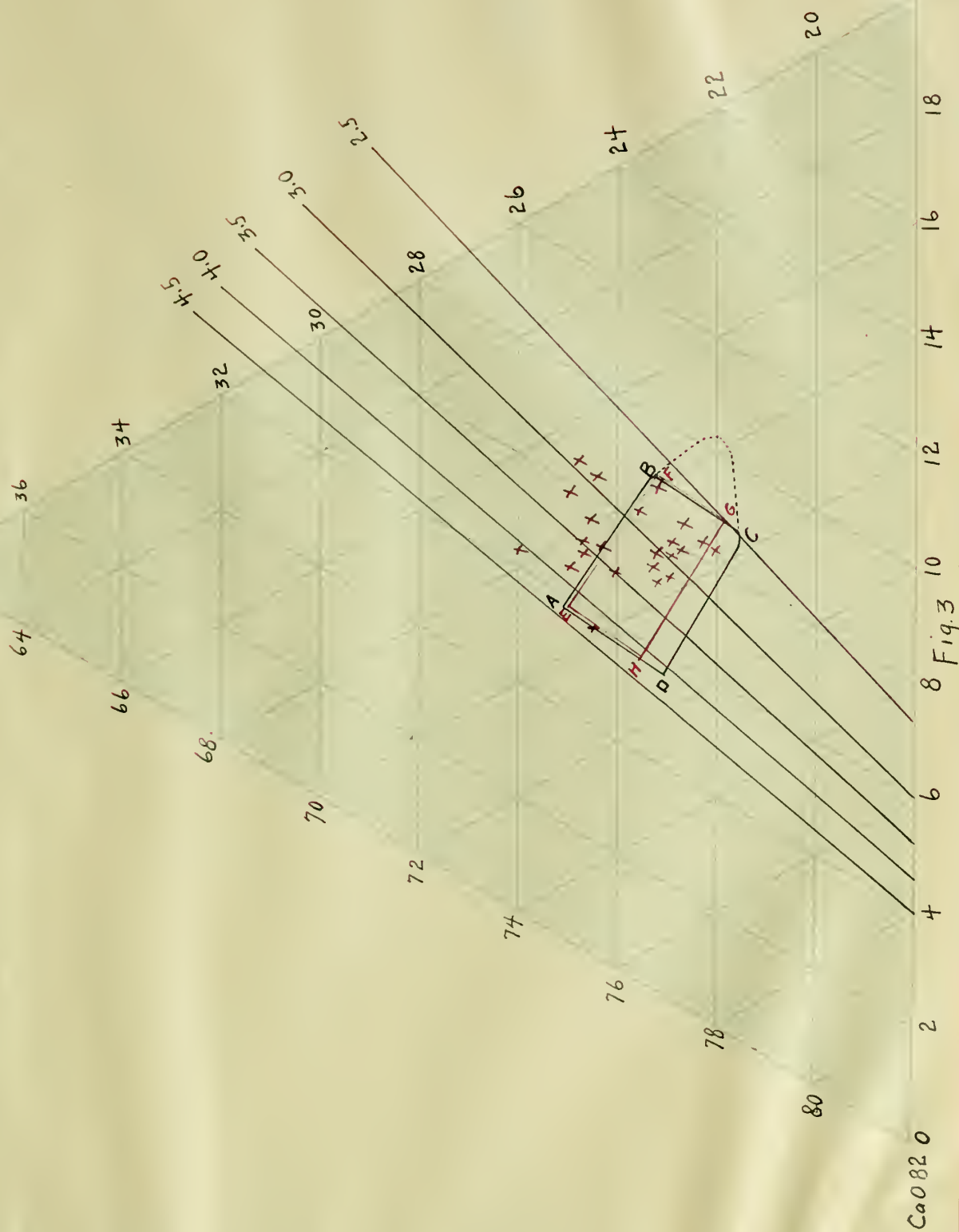
Tensile Strength in lbs. - 7 days test.

	1.	2.	3.	4.	5.
a.	No strength	No Strength	No strength	No strength	160
b.	"	"	"	"	158
c.	"	"	"	"	<u>162</u>
Av.					160
	6.	7.	8.	9.	10.
a.	195	No strength	No strength	215	188
b.	222	"	"	218	200
c.	<u>229</u>	"	"	<u>221</u>	<u>210</u>
Av.	215			215	199
	11.	12.	13.	14.	15.
a.	138	227	190	320	145
b.	131	238	168	310	165
c.	<u>142</u>	<u>233</u>	<u>204</u>	<u>280</u>	<u>154</u>
Av.	<u>137</u>	<u>236</u>	<u>184</u>	<u>303</u>	<u>154</u>

CoO 62 SiO₂ 38






$$\begin{array}{l} 18\text{SiO}_2 \\ 20\text{Al}_2\text{O}_3 \end{array}$$

DISCUSSION OF RESULTS

Among the clinkers No. 6 was the only one which did not show dusting. Nos. 9, 10, 11, and 12 did not dust as badly as the rest, Nos. 1, 2, and 7 being the worst of the series.

In the boiling test No. 6 was found to be firm and hard, and showed no cracking or disintegration. Nos. 9, 10 and 12 cracked slightly and were somewhat soft but did not disintegrate. No. 11 withstood the test fairly well but was inferior to those above mentioned.

Although Nos. 6, 9, 10, 11 and 12 are considered to be good cements yet their tensile strengths were found to be comparatively low. This may be due to the lack of sufficient fluxing material in the batch or to the fact that the clinkers were not quenched with water.

In Fig. 2 a section of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ is plotted on a large scale, the rectangle vxyz being the field shown by Shepherd and Rankin as the approximate range of composition of Portland cements. The mixtures used in the present study are plotted and the rectangle ABCD is drawn to show the probable field of good composition for Portland cements as determined by the boiling tests. The tensile strength tests show all the mixtures enclosed in this field to be of good strength. No. 11 which showed a fair boiling test is very low in strength and is therefore not included in the field. No. 14 shows the highest strength of any of the mixtures but failed in boiling test. It is probable that its high Al_2O_3 content is the cause of its early strength but its failure in the soundness test suggests that it would probably depreciate in strength after a longer period of time as is charac-

teristic of high Al_2O_3 contents.

In Fig. 2 the field of work of Bleininger is plotted and his field of sound cements enclosed in the red ink rectangle EFGH. The two fields correspond quite well although Bleininger's is somewhat narrower.

In Fig. 3 both fields have been plotted and lines showing various percentage ratios of $\text{SiO}_2 : \text{Al}_2\text{O}_3$. Both diagrams show definite limits in this ratio of 2.5 to about 4.4. Bleininger states that 3.1 to 4.1 are the best but commercial cements frequently run as low as 2.5. The composition, (referred to CaO , Al_2O_3 , and SiO_2) for a number of commercial cements have been plotted and show a majority to fall within the field shown in this study. Those showing a much lower lime content are doubtful as to the correctness of analysis.

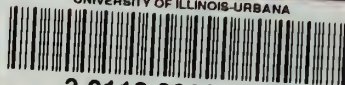
Good cements may be made with a $\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$ ratio by percentage of 2.5- 4.4.

The batches for good cements may be well calculated by a formula close to Bleininger's (2.8 CaO SiO_2) + ($2 \text{ CaO}.\text{Al}_2\text{O}_3$).





UNIVERSITY OF ILLINOIS-URBANA



3 0112 086830293